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$U^{3+}/LiYF_4$, a promising IR laser

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Abstract: *Under reducing conditions, single crystal of $LiYF_4$ doped with 762 ppm of U^{3+} were obtained. Absorption and fluorescence spectra of this system are presented as well as the energy level scheme of the lasing transition. Oscillator strength and laser cross section between Stark levels of the $^4I_{11/2} \rightarrow {}^4I_{9/2}$ transition are calculated.*

1- Introduction

Recently crystal of $LiYF_4$ (YLF) activated with Er^{3+} ions were greatly investigated as active material generating stimulated emission of erbium ions in the region of 2.7 μm [1]. U^{3+} has a $5f^3$ configuration and is isoelectronic with Nd^{3+} ion ($4f^3$). Trivalent uranium in CaF_2 have been greatly studied in the early sixties for his potential use as infrared laser [2]. It has now a renewed interest because it possesses, like erbium, an excited state around 0.8 μm and 0.9 μm which can be pumped by a diode and an efficient emission which takes place between 2 μm and 2.9 μm [3] at room temperature. However U^{3+} is not the most stable valence of uranium ion. The first studies of U doped YLF have been done by G. J Quale et al [4] and M. D. Jensse et al [3]. The authors show that U/YLF is a promising IR laser, however the color of the crystal (pale green) and the absorption spectra show that U is predominantly tetravalent. In fact single crystals of U/YLF grown by Czochralsky method by one of us are pale green and optical absorption spectra in UV, Visible and IR at room temperature and liquid helium temperature are characteristic of tetravalent uranium [5].

In this paper we report on the optical spectra (absorption and fluorescence) corresponding to pure trivalent uranium after reducing conditions, oscillator strength and laser cross section of the $^4I_{11/2} \rightarrow {}^4I_{9/2}$ transition.

2- Experimental procedure

Several U doped YLF single crystals were grown by Czochralsky method with different concentrations of uranium (500-2000 ppm). The obtained crystals with laser optical quality

have a pale green color characteristic of tetravalent uranium [5]. The U concentration on a reference crystal was obtained by HF induced plasma emission spectrometry (500ppm). The concentration of all samples was deduced from this reference by comparing the absorption coefficient.Then the reduction of U^{4+} ions to U^{3+} was ensured by submitting samples to highly ionizing radiations (^{60}Co: 1.17-1.33 Mev - X photon :17.5 kev) [6].

Absorption spectra of single crystals were recorded at 300K and 10K on a Cary 17 double beam spectrophotometer from 1900 up to 2500 nm, using a cryogenic cryostat. The IR emission of the U^{3+}/YLF at 300K was analysed with a spectrophometer Jobin-Yvon HR1000 whose dispersion is 8A/mm. A PbS photoresistor was used as detector. The luminescence spectrum was obtained by exciting either with a 100W iodide lamp or a YAG laser pumped dye laser in the f-d transitions.

3-Results and discussion

A pale green sample doped with 762 ppm of U^{4+} submitted to the γ radiations of a ^{60}Co source during 48 hours becomes orange-brown. The absorption spectra at 10K of this sample, after irradiation, is shown Fig 1. Very intense absorption lines between 0.3 μm and 0.55 μm are characteristic of the f-d transitions of U^{3+} [7], while the absorption narrow lines between

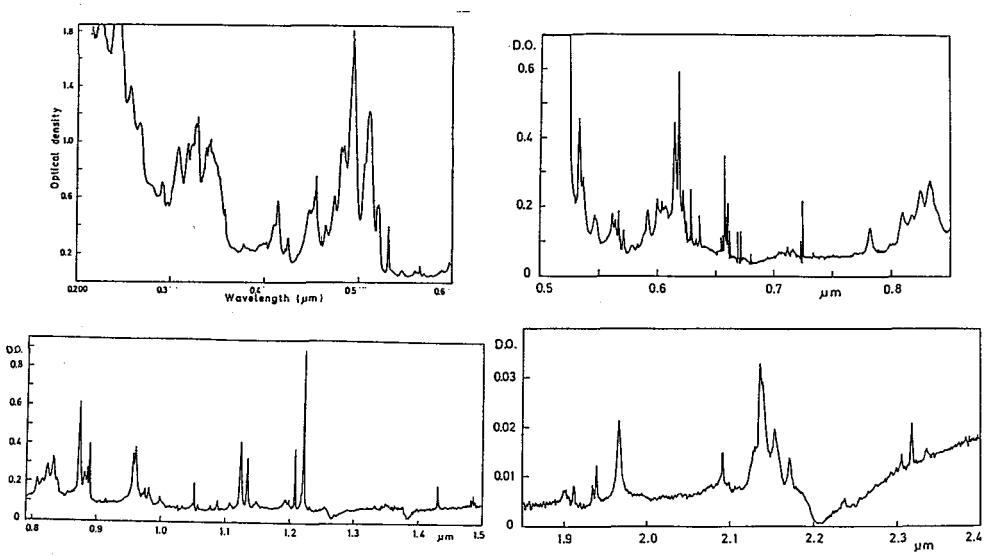

Fig. 1- Absorption spectra of $U^{3+}/LiYF_4$ at 10K (DO of the spectrum 0.2-0.6 μm must be multiplied by 2.7)

1.9 μm and 2.2 μm correspond to $^4I_{9/2} \rightarrow {}^4I_{11/2}$ transition responsible for the IR emission between 2 and 2.9 μm. All the lines observed in the pale green crystal have disappeared

completely, which shows that 100% of U has been reduced in U^{3+} after γ irradiation.

From the absorption spectra of the $^4I_{9/2} \rightarrow {}^4I_{11/2}$ transitions at room temperature, the oscillator strength of some transitions between Stark levels can be evaluated by measuring the area of the bands corresponding to the transitions from the ground state to the Stark excited states of the $^4I_{11/2}$ multiplet: $1 \rightarrow 1$, $1 \rightarrow 3$, $1 \rightarrow 4$ and $1 \rightarrow 6$ following the expression

$$f = \frac{nmc^2}{N_0 \pi e^2} \left(\frac{3}{n^2+2}\right)^2 \int \alpha(\nu^*) \delta\nu^*$$

Here m and e are the mass and the charge of the electron, c the vacuum velocity of light, n the refractive index (1.47) at the transition wavelength, α the absorption coefficient, ν^* is the wave number, and N_0 is the number of ions per cm^3 ($1.067\ 10^{19}$).

The oscillator strengths between the ground state of $^4I_{9/2}$ multiplet and Stark levels of the $^4I_{11/2}$ multiplet are represented in the table I:

Table I: Oscillator strength between Stark levels of the $^4I_{9/2} \rightarrow {}^4I_{11/2}$ transition

$^4I_{9/2} \rightarrow {}^4I_{11/2}$	$f_{1\text{-}1}$	$f_{1\text{-}3}$	$f_{1\text{-}4}$	$f_{1\text{-}6}$
$x10^{-7}$	1.84	10.7	5.69	2.82
λ_0 (µm)	2.235	2.144	2.09	1.97

The analysis of the polarised fluorescence and absorption spectra at 300K and 10K already described elsewhere [5], permit to establish the Stark energy scheme for the ground and for the first metastable manifolds $^4I_{9/2}$-$^4I_{11/2}$. Fig2).

The ground state splitting of U^{3+} in YLF (1113 cm^{-1}) is very large compared to the one obtained for CaF_2 [8] (609 cm^{-1}) or for the ZBLAN (660 cm^{-1}) [9], which makes this material more promising that CaF_2 or ZBLAN.

The applicability of $LiYF_4$ as a laser source with U^{3+} ions around 2.2 µm can be estimated from the laser cross- section

The fluorescence and absorption spectrum of the $^4I_{11/2} \rightarrow {}^4I_{9/2}$ transition at

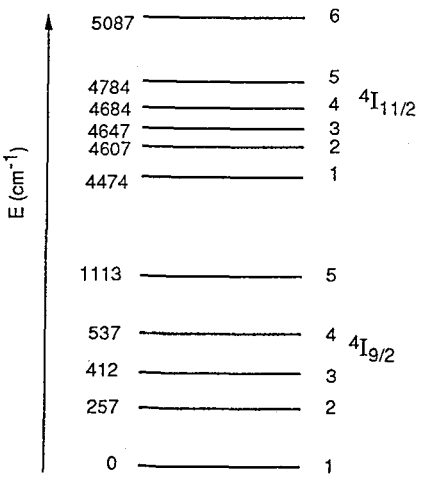

Fig. 2- Stark energy level scheme for $^4I_{11/2} \rightarrow {}^4I_{9/2}$

300 K are reported in Fig. 3. From the absorption coefficient of the $^4I_{9/2} \rightarrow {}^4I_{11/2}$ transition at 2.235 μm corresponding to the 1→1 transition (see Fig2), we have calculated the room temperature cross section to be 1.4 10^{-20} cm^2.

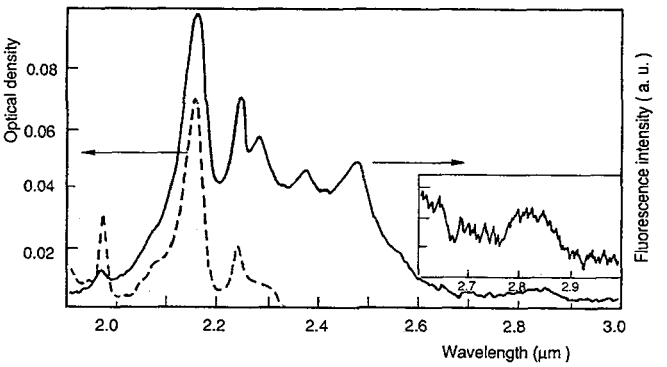

Fig. 3. Fluorescence and absorption spectra of $U^{3+}/LiYF_4$ at 300K

This value is relatively high compared to the cross section obtained for $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition of Er^{3+} at 2.72 μm [1] (3. 10^{-21} cm^2), and makes this system promising for an IR laser .However this value is about ten times less than the one predicted by H. P. Jenssen and al. This discrepancy comes mainly from the fact that the authors just give an estimate of the U^{3+} concentration since they have both valence states $U^{3+}$and U^{4+} in their crystal.

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